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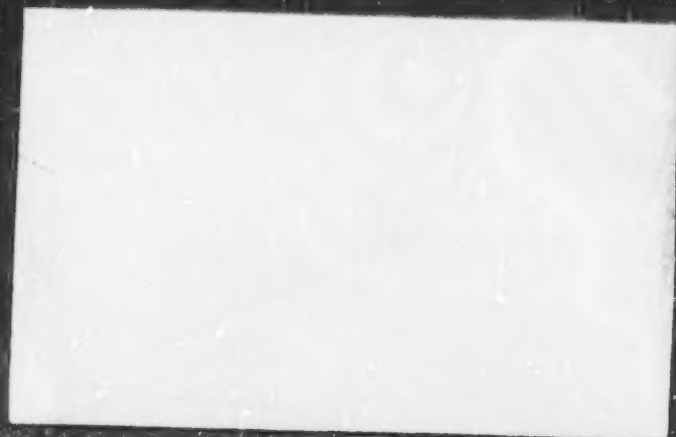
THE ALSTERBERG (AZID) MODIFICATION OF THE WINKLER
METHOD FOR THE DETERMINATION OF THE BOD OF
INCINERATOR QUENCH WATER AND THE CALIBRATION OF
THE WESTON AND STACK DO ANALYZER MODEL 300-B

BUREAU OF SOLID WASTE MANAGEMENT

1970

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OF THE WINKLER METHOD
FOR THE DETERMINATION OF THE BOD
OF INCINERATOR QUENCH WATER
AND THE CALIBRATION
OF THE WESTON AND STACK DO ANALYZER
MODEL 300-B

A Division of Research and Development
Open-File Report (RS-03-68-17)

written by
DONALD L. WILSON, Research Chemist

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
Bureau of Solid Waste Management
1970

PREFACE

In publishing an analytical method which employs specific brands of laboratory supplies and instrumentation, the U.S. Public Health Service does not imply that other commercial products could not be utilized with appropriate modifications in the procedure.

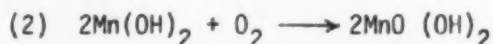
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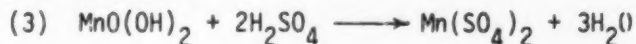
DISCUSSION

The Winkler method developed in 1888, is the routine chemical method for the determination of dissolved oxygen. The basic procedure involves the oxidation of manganous hydroxide (Mn^{++}) by the oxygen, dissolved in the water, to manganic hydroxide:



Manganous hydroxide is a white flocculant precipitate which changes to light brown when oxidized. Since the reaction with the oxygen must occur on the surface of the floc particles, physical mixing at this point is important.

When manganic hydroxide is acidified, manganic sulfate is formed:



In the presence of iodide, the manganic salt acts as an oxidizing agent, releasing free iodine:

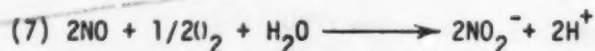


The iodine, which is stoichiometrically equivalent to the DO of the sample, is titrated with thiosulfate:



For convenience, the alkali (equation 1) and the iodide (equation 4) are combined into a single alkaline-iodide reagent.

The original Winkler method has been modified since oxidizing agents give a positive interference, reducing agents a negative interference, and organic compounds a varied interference. The most common interference is that caused by nitrites, commonly present in polluted waters and wastes. The nitrite ion reacts with iodides, as follows:



The Alsterberg (Azide) Modification utilizes sodium azide to reduce the nitrites, in the following manners:



The Alsterberg (Azide) Modification of the Winkler Method utilizing "dilution water" is employed to standardize the Weston and Stack DO Analyzer. However, before the method can be utilized to determine the BOD of incinerator quench water, the samples must be analyzed for the presence of interfering substances. If the final diluted sample contains more than 4 ppm nitrite, or 1 ppm ferrous iron, or 200 ppm ferric iron, or any sulfite or thiosulfate, or large amounts of chloride, which may evolve as chlorine during the analysis, the Alsterberg Modification can not be employed. If however, the final diluted sample contains less than 4 ppm nitrite or 1 ppm ferrous iron or 50 ppm ferric iron, valid results can be obtained using the procedure. In addition, samples containing residual chlorine, 50 to 200 ppm ferric iron, or having a pH less than 6.5 or greater than 8.3, can also be evaluated using certain alterations of the procedure.

The preliminary tests presented herein (appendix), can be employed to evaluate the applicability of the Alsterberg (Azide) Modification in the determination of the BOD of a quench water sample. Since the tests are qualitative and involve distinct color changes or precipitates, the concentration of the reagents may be approximate. Standards should be employed, however, to verify the validity of the preliminary analyses and impart to the analyst knowledge of the color intensity and hue.

Since the tests are not specific and hence give a positive reaction in the presence of several substances, they are assigned group numbers. Each of the interfering substances, mentioned earlier, does however fall in one of the groups.

APPARATUS

All glass and plastic apparatus must be cleaned thoroughly to assure the removal of all materials capable of exerting a BOD. Detergents may be utilized if cleaning is followed by thorough rinsing with distilled water.

The apparatus requirements are as follows:

1. Incubation (BOD) bottles, 300 ml capacity.
2. Air incubator or water bath, thermostatically controlled at $20\text{C} \pm 1\text{C}$.
3. Buret - 50 ml.
4. 200 ml volumetric flasks specially marked for 203 ml.
5. Graduates - 10 ml, 50 ml, 1 liter, and 2 liter.
6. Volumetric flask - 100 ml, 500 ml, 1 liter.
7. Mohr pipets - 10 ml with 1 ml divisions
8. Carboys, two - 7 liters or more, polyethylene nalgene, wide mouth.

9. Reagent Bottles - 1 liter, narrow mouth, ground glass stoppers.
10. Erlenmeyer flasks - 500 ml.
11. Beakers - 250 ml, 2 liter, and 3 liter.
12. Siphon tubing
13. Balance - Analytical (also Trip, if available).
14. pH paper - range 2 to 9.
15. Sample collection bottles, polyethylene (or similar non-breakable containers), narrow mouth, tightly fitting caps, about one liter, sterile (no material present which has a BOD value).
16. Magnetic stirrer with Teflon^(R) coated stirring bar.
17. Ice chest, capable of holding several one liter sample collection bottles and maintaining a 5C temperature for 24 hours.

REAGENTS

Chemical Requirements

The following chemicals are ACS, Reagent grade:

1. phosphate buffer solution, pH 7.2 (or prepared)
2. potassium phosphate, monobasic
3. potassium phosphate, dibasic
4. sodium phosphate, dibasic, heptahydrate
5. ammonium chloride
6. magnesium sulfate, crystal
7. calcium chloride, anhydrous
8. ferric chloride, lump
9. sodium hydroxide or potassium hydroxide

10. sodium iodide or potassium iodide
11. sodium azide
12. sulfuric acid, concentrated
13. manganese(ous) sulfate, monohydrate (may be other hydrates).
14. Thyodene
15. sodium thiosulfate, crystal
16. chloroform
17. potassium biniodate, solid or 0.025N solution, or potassium dichromate
18. potassium fluoride

Preparation of Solutions

All solutions are prepared with distilled water which was distilled from a block tin or all-glass still, contains less than 0.01 mg/l copper, and free of chlorine, chloramines, caustic alkalinity, organic materials, and acids. The solutions are prepared in the following manner:

1. Standard sodium thiosulfate solution - 0.025N: Dissolve exactly 6.205g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Preserve by adding 5 ml of chloroform. Note: a) This solution is equivalent to 0.200 mg DO per 1.00 ml. When employed to titrate 203 ml of treated sample (200 ml of original sample), each ml is then equivalent to 1 mg/l (ppm) DO in sample. b) This solution is not stable more than 9 days (see Standardization).
2. Standard potassium biniodate solution - 0.025N (if not purchased): Dissolve 0.8124g KHIO_3 in distilled water and dilute with same to one liter.

3. Standard potassium dichromate solution - 0.025N (if standard potassium biniodate solution not available): Dissolve 1.226g $K_2Cr_2O_7$ (previously dried for 2 hours at 110C) in distilled water and dilute with same to one liter.
4. Sodium hydroxide solution, approximately 1N: Dissolve 41.6g NaOH in distilled water and dilute with same to one liter.
5. Sulfuric acid solution, approximately 1N: Cautiously add 28 ml of concentrated H_2SO_4 to distilled water and dilute with same to one liter.
6. Phosphate buffer solution, pH 7.2 (if not purchased): Dissolve 8.5g KH_2PO_4 , 21.75g K_2HPO_4 , 33.4g $Na_2HPO_4 \cdot 7H_2O$, and 1.7g NH_4Cl in 500 ml of distilled water and dilute with same to one liter. The pH of this buffer should be 7.2 without further adjustment.
7. Magnesium sulfate solution: Dissolve 22.5g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute with same to one liter.
8. Calcium chloride solution: Dissolve 27.5g anhydrous $CaCl_2$ in distilled water and dilute with same to one liter.
9. Ferric chloride solution: Dissolve 0.25g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute with same to one liter.
10. "Dilution Water": Place 7 liters of distilled water in polyethylene, wide mouth, carboys (other volumes and containers may be used). Add 7ml (1 ml per liter of water) of each of the following prepared solutions: Phosphate buffer, pH 7.2; magnesium sulfate; calcium chloride; and ferric chloride. Before being used this water should be at 20C.

11. Alkali-iodide-azide reagent: Dissolve 500g NaOH (or 700g KOH) and 135g NaI (or 150g KI) in distilled water and dilute to 1 liter. To this solution add (10g NaN_3 dissolved in 40 ml of distilled water) with constant stirring. This reagent should not give a color with Thyodene indicator when diluted and acidified.
12. Manganese sulfate solution: Dissolve 480g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (or 400g $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ or 364g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$) in distilled water, filter, and dilute to 1 liter.
13. Potassium fluoride solution: Dissolve 40g $\text{KF} \cdot 2\text{H}_2\text{O}$ in distilled water and dilute to 100 ml.

SAFETY PRECAUTIONS

Follow general laboratory safety rules. This method has no pronounced safety hazards. However, care must be taken when handling the concentrated sulfuric acid. A pad of tissue held over the BOD bottles when they are inverted will prevent splatter of treated sample which might leave stains and harm the analyst hand.

STANDARDIZATION

With sodium thiosulfate prepared exactly no standardization is needed. Standard sodium thiosulfate solution, exactly 0.025N, is equivalent to 0.200mg DO per 1.00 ml or when 203 ml of the treated sample is titrated with 0.025 N thio:

$$1 \text{ ml } 0.025 \text{ N thio} \equiv 1 \text{ mg/l DO}$$

However, a sodium thiosulfate solution is not stable and solutions over 9 days old must be standardized with a biniodate (preferred) or dichromate standard 0.025N solution.

The procedure for standardization is as follows:

<u>Procedure</u>	<u>Comments</u>
1. Dissolve approximately 2g of KI in a 500 ml erlenmeyer flask with 150 ml of distilled water.	1. May use trip balance, if available.
2. Add 10 ml of dilute sulfuric acid	2. 1 part conc. H_2SO_4 and 9 parts distilled water.
3. Add 20 ml of standard solution	3. Biniodate or dichromate.
4. Dilute to 300 ml with distilled water.	4. If dichromate standard solution used, put flask in dark for 5 minutes.
5. Titrate the liberated iodine with standardized thiosulfate titrate to a pale straw color.	
6. Add about 1/2 g of Thyodene indicator and shake flask.	6. After Thyodene is added, a blue color appears.
7. Continue titrating until blue color disappears.	
8. Record the amount of titrant used.	
9. Repeat steps #1-8 for a second test.	9. The absolute value of the difference between duplicated readings should not exceed $1.96\sqrt{2}s$, or 0.36 ppm, more than 5% of the time. See "Precision".

ANALYSIS OF SAMPLES

Sample Collection

Site Selection. When the BOD of quench water is measured to determine the amount of oxidizable wastes that will be discharged to a sewerage system serving an incinerator facility or a drainage system associated with the residue disposal area, the site of sample collection must be chosen with due consideration. Settlement tanks, surface pools, sewers, and other areas immediately adjacent to the sewerage or drainage system are preferable collection sites.

Sample Size and Container. Normally 50 ml of sample is needed to perform the BOD analysis; however, since various dilutions may be needed and a larger sample size may be more representative, it is recommended to collect one liter quench water sample.

The samples should be collected in sterile, non-breakable bottles with narrow mouths and caps which can be tightly fitted. The sample bottle should be completely filled. All containers must be thoroughly rinsed, especially if cleaned with a detergent, before they can be reused.

Samples should not be collected on Monday or Tuesday unless the analysts are to work on Saturday or Sunday (5-day BOD).

Sample Preservation and Shipment

If the sample analysis is to be initiated within four hours after collection, sample preservation measures are not absolutely necessary.

However, if initiation of the analysis will be started after four hours, samples, soon after collection, should be placed in an ice chest (or similar container) so that the samples are maintained in the dark at 5C. The bottle caps must be tightly fitted to prevent an increase in oxygen solubility with the reduction in temperature.

Sample shipment to the laboratory should be immediate and via air freight if necessary to insure the initiation of BOD analysis in the laboratory within 24 hours of sample collection. Samples received after 24 hours old should not be analyzed. Because samples require some preparation before the actual analysis and the exact dilution requirements may not be known, samples (not at 5C) should be shipped to the laboratory so that they are received two to four hours (depending upon number of samples and laboratory personnel) before the end of the normal working day. Samples shipped in an ice chest (5C) and refrigerated may be analyzed the following day provided the analysis can be initiated before the samples are 24 hours old.

SAMPLE (AND BLANK) PREPARATION

Adjustment for Nitrification Process

Prior to analysis each sample (and "dilution water" blank) is treated as follows to inhibit the nitrification process:

<u>Procedure</u>	<u>Comments</u>
1. Place 50 ml of a thoroughly mixed quench water sample in a 250 ml beaker.	1. The exact volume of quench water sample depends upon the dilution requirements. See "Dilution and Aeration"
2. Using pH paper, check the pH of the sample.	2. Usually the pH is about 11.
3. Using 1N NaOH or 1N H ₂ SO ₄ adjust the pH of the sample to a range of 2 to 3; maintain pH for 15 minutes.	3. Omit if the sample already has a pH of 2 to 3.
4. Then neutralize the sample to a pH of 6.5 to 8.3.	4. Employ the same 1N solutions as in step 3.

Adjustment for Residual Chlorine. Since residual chlorine dissipates when samples stand for 1 to 2 hours or they are well aerated, no adjustments are therefore recommended.

Dilution and Aeration. Prepared samples must be diluted in order to obtain a measurable depletion (2 ppm to 7 ppm) of oxygen at the end of the 5-day incubation period. Since incinerator quench water usually has a BOD of 100-300 ppm, a suitable or applicable dilution is 50 ml of sample diluted to 2 liters. If the analyst suspects that the BOD of the quench water differs from the usual value, he should test various dilutions since the analysis cannot be repeated upon the same original sample after the 5-day waiting period. To obtain more reliable results, 5 BOD bottles should be prepared, two for the initial DO (can be

immediately repeated if necessary) and three for the final DO (only two reasonable results are needed), and the final DO values should never be less than 1.0 ppm.

Since the dilution water, employed in the analysis of each quench water, may contain a few oxidizable materials capable of exerting a small BOD, each quench water analysis should include a blank evaluation, i.e., a determination of the BOD of the dilution water. The observed BOD of the quench water can then be corrected by subtracting the appropriate proportionate fraction of this blank value.

The dilution and aeration procedures are as follows:

<u>Procedure</u>	<u>Comment</u>
1. Pour the total prepared sample from the 250 ml beaker into a 2 liter graduate and dilute to the mark with "dilution water."	1. Solution still represents 50 ml of original sample.
2. Aerate the sample by pouring it forth and back from the graduate into a 3 liter beaker at least 3 times.	2. Dilution water blank is aerated in like manner.
3. Siphon the diluted aerated sample (or blank) from the beaker and into 5 BOD bottles.	3. The sample should be stirred continuously using a magnetic stirrer and a Teflon [®] coated magnetic bar.

4. The DO concentration of the sample (or blank) in 2 BOD bottles should be determined immediately.
 4. a) See "Determination of the DO Concentration."
 - b) At least, two reasonable DO results are needed. See "Precision."
5. Then put the remaining 3 BOD bottles in an incubator (or waterbath) and determine their DO content after a 5-day incubation period at 20C.
 5. a) During the incubation period the samples should not be exposed to the light.
 - b) See "Determination of the DO Concentration."
 - c) Only two reasonable DO results are needed. See "Precision."

Determination of the DO Concentration

Procedure

1. To each BOD sample bottle, add 2 ml of manganous sulfate solution and then 2 ml of alkaline-iodide-azide reagent.

Comments

1. a) When a sample is being evaluated for the purpose of DO probe calibration, the probe determination of the DO content must precede that by this Winkler Method. See DO Analyzer Method (Bibliography).
- b) The tip of each pipette must be below the surface of the sample.

2. Replace the stopper, exclude air bubbles, and mix by inverting 9-10 times.
3. When the precipitate settles, repeat the inverting and settling.
4. After about 100 ml of clear supernate, remove stopper and immediately add 2 ml of conc. H_2SO_4 above surface of the sample.
5. Stopper the bottle and mix to dissolve the precipitate.
6. By means of a modified 200 ml volumetric flask, transfer 203 ml of the treated sample to a 500 ml erlenmeyer flask.
7. Titrate the treated aliquot with standardized thiosulfate titrant to a pale straw color.
8. Add about 1/2 g of Thyodene indicator and shake flask.
9. Continue titrating until blue color disappears.
10. Record the amount of titrant used.
2. A kimwipe pad held over the top of the bottle helps prevent splattering.
4. If the diluted sample contains more than 50 ppm ferric iron, add 1 ml of KF solution before the acid.
- 6.a) Volume adjusted for the 4 ml of reagents added (See Calculations).
- b) Transfer 204 ml if KF solution used.
8. After Thyodene is added, a blue color appears.

11. Repeat steps #1-10 with each BOD sample bottle.

- 11.a) Titration values less than 1.0 ml should be disregarded.
- b) The absolute value of the difference between duplicated readings should not exceed $1.96/\sqrt{2}$ s, or 1.35 ppm, more than 5% of the time. See "Precision."

CALCULATIONS

Sample Volume to be Titrated

Since a portion of the sample in the BOD bottle is displaced during the analysis due to the addition of reagents, the volume of sample to be titrated must be adjusted to compensate for this loss. The required volume is calculated as follows:

$$V_1 = 200 \left(\frac{V_2}{V_2 - V_3} \right)$$

Where: V_1 = The volume of sample to be titrated

V_2 = The volume of BOD bottle employed

V_3 = The volume of reagents added

(The volume of the sulfuric acid added is not included since the acid only displaces sample which has been deoxygenated).

Dissolved Oxygen Content of Sample

The dissolved oxygen content of a sample is calculated as follows:

$$D = FV_4$$

Where: D = The dissolved oxygen content of the sample
being titrated

F = The correction factor, ratio of normality
of standard (thiosulfate) to 0.025 (normality
of biniodate or chromate)

V_4 = The volume of sodium thiosulfate used to
titrate the sample

BOD of Sample

Dilution Water Sample. The following formula should be employed
to calculate the BOD of each individual sample of "dilution water."

$$BOD_1 = D_1 - D_2$$

Where: BOD_1 = The biochemical oxygen demand of dilution
water

D_1 = The dissolved oxygen content of initial (before
incubation) dilution water

D_2 = The dissolved oxygen content of final
(after incubation) dilution water

Quench Water Sample. The initial DO concentration minus the final
DO concentration equals BOD of the diluted sample. The BOD of the
diluted sample times the dilution factor equals the BOD of the original
sample.

The dilution factor is found by dividing the original amount of sample taken into the final dilution as: 50 ml of sample diluted into 2 liters gives a factor of 40.

The following formula should be employed to calculate the BOD of each individual sample of quench water.

$$BOD_2 = F[(D_3 - D_4) - P_1(BOD_1)]$$

Where: BOD_2 = The biochemical oxygen demand of quench water

F = The dilution factor

D_3 = The dissolved oxygen content of initial (before incubation) quench water

D_4 = The dissolved oxygen content of final (after incubation) quench water

P_1 = The decimal fraction of dilution water used in the BOD analysis of the quench water.

METHOD EVALUATION

Precision

After analyzing a number of "quench water" samples, in duplicate (three final DO determinations were performed to ensure reasonable duplicate results), the precision of the observations were evaluated by calculating (using Olivetti Programma 101) the pooled standard deviation of all observations, except those obtained on samples collected from dump truck drainage.

The results of these calculations are shown in the following table.

Accuracy

There is no standard against which the accuracy of the BOD test can be measured.

Sensitivity

This Alsterberg (Azide) Modification of the Winkler Method is not applicable to samples with a dilution factor of 40, having a 5-day BOD value of 54.1 ppm or less.

TABLE 1 - PRECISION OF THE DO AND BOD ANALYSES

Type of Sample	Type of Analysis	No. of Determ.	"S" ^a	Dilution Factor ^b	Confidence Range ^c or $\pm (S)(1.96)(40)$
Standards (normality)	DO	44	0.13 ^d	--	--
Dilution Water (Blank)	DO	32	0.19	--	--
	BOD	--	0.27	40	<u>+21.2</u>
Quench Water	DO	76	0.49	--	--
	BOD	--	0.69	40	<u>+54.1</u>
Both Dil. and Quench Water	DO	108	0.43	--	--
	BOD	--	0.61	40	<u>+47.8</u>

^aFor DO analysis, "S" is pooled standard deviation. For each BOD analysis "S" is an estimate of the standard deviation of differences between two DO readings (i.e. $S = \sqrt{s^2 + s^2}$.)

^bDilution factor may vary but for calculation purposes the normal dilution factor is shown here.

^c95% confidence limits about a single BOD result, assuming a standard dilution factor of 40 or 2.5 percent dilution.

^dThe absolute value of the difference between duplicated readings should not exceed $1.96/2s$, or 0.36 ppm, more than 5% of the time.

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APPENDIX

QUALITATIVE TESTS FOR THE DETERMINATION
of the
PRESENCE OF INTERFERING SUBSTANCES IN QUENCH WATER

INTRODUCTION

Principle of Tests

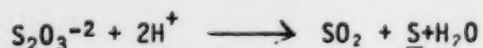
These qualitative tests may be employed as a quick means of detecting the presence of oxidizing or reducing substances (as sulfites, nitrites, ferrous and ferric salts, residual chlorine) which will interfere with the Modified Winkler Method for the determination of BOD (Table 1).

Although the presence of sulfate does not affect the Modified Winkler Method, the presence of large quantities of it may indicate the possible presence of sulfite which definitely affects the method. Likewise, large amounts of chlorides may indirectly affect the method by releasing chlorine gas during acidification.

The principle of each of these tests is discussed briefly in the following sections.

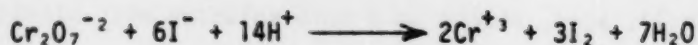
Test for Group A Substances (as sulfates). When a barium chloride solution is added to a solution, containing a sulfate type material, an insoluble white precipitate, as barium sulfate, will form. This precipitate can be detected visually.

Test for Group B Substances (as thiosulfate, sulfite). Thiosulfate will react with mineral acids to yield insoluble elemental sulfur.



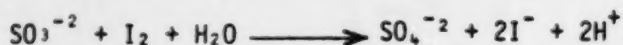
The presence of thiosulfates can then be detected when a pale-whitish-yellow precipitate forms after the addition of acid.

In the presence of an acid, dichromate will oxidize iodide to iodine which will then impart a blue color to the solution when Thyodene is present.



Sulfite-like material may be detected by first treating a sample with an acid-iodide solution, a small amount of Thyodene powder, and then perform a dropper-titration using potassium dichromate solution. If sulfite-like material is present in the sample, the volume of dichromate solution required to obtain a blue solution then yellow-dichromate color will exceed that required by a reagent blank solution.

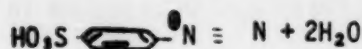
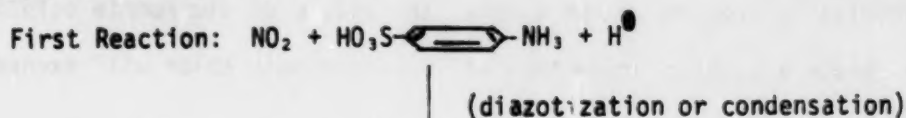
Small amounts of sulfite can be detected in the presence of any amount of thiosulfate because on oxidizing a sulfite-thiosulfate mixture with iodine (Neutral solution):



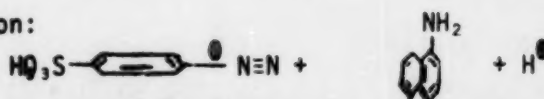
hydrogen ions are formed only in the case of sulfite. The resulting acidity can be revealed by litmus paper.

The presence of sulfite-type substances in a sample can produce false negative results with the tests for interferences similar to nitrite, ferrous iron, ferric iron, and residual chlorine in effects. However, since no amounts of sulfite-type materials can be present in a sample, a positive test for sulfite-type compounds eliminates the need for performing the other tests for interferences.

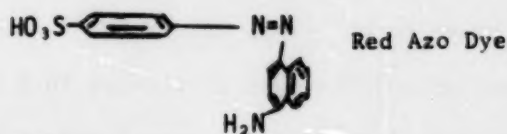
Test for Group C Substances (as nitrites). The primary aromatic amine, sulfanilic acid, reacts in an acid solution with nitrites to form diazonium cations which subsequently couple with 1-naphthylamine[may substitute with 1-naphthylamine hydrochloride or N-(1-naphthyl)-ethylenediamine dihydrochloride] to form the red p-benzene sulfonic acid-azo- α -naphthylamine. The red color is then indicative of the presence of nitrite-type substances.



Second Reaction:

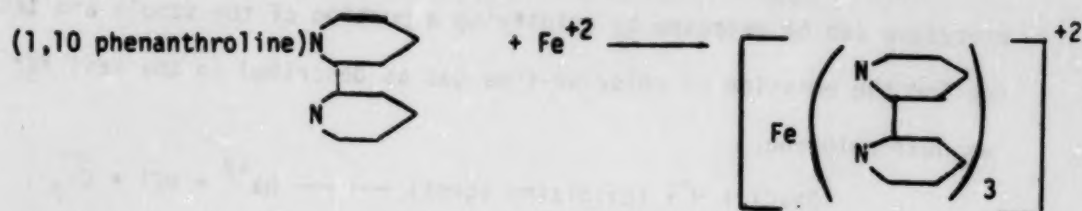


↓
coupling (electrophilic aromatic
(substitution) (Occurs with phenols
in alkaline solutions)



Test for Group D Substances (as ferrous salts). In the presence of an acid solution, ferrous salts will react with 1,10 phenanthroline to form a pale orange-red complex, however, sometimes the sample may have to be filtered to detect the color. More expensive 1,10 dipyridyl can be

substituted for the 1,10 phenanthroline. The organic base 1,10 dipyridyl reacts with ferrous iron to form a deep red very stable complex cation.



Ferric salts do not react under these conditions; consequently very small amounts of ferrous salts can be detected in the presence of large proportions of ferric salts.

Test for Group E Substances (as ferric salts). Ferric salts are reduced by hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) to ferrous salts and allowed to react with 1,10 phenanthroline in the test for Group D. A more intense orange-red color than found in the test for Group D indicates the presence of ferric-type substances.

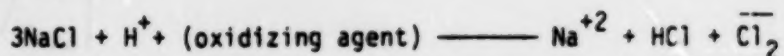
Test for Group F Substances (as residual chlorine). The presence of chlorine can be detected indirectly by its oxidation of iodide to iodine and the subsequent formation of a blue color in the presence of Thyodene.



Test for Group G Substances (as Chlorides). The presence of chlorides can be detected by the addition of silver nitrate to a portion of the sample solution. If chloride-type substances are present, a white precipitate will form.



Test for Group H Substances (as released chlorine). The presence of chlorine gas that is liberated during analysis by the Alsterberg-Winkler procedure can be detected by acidifying a portion of the sample and testing for the emission of chlorine-type gas as described in the test for residual chlorine.



SENSITIVITY OF TESTS

These qualitative tests have the following sensitivities:

sulfate	> 0.5 ppm
thiosulfate	> 1.0
sulfite	> 1.0
nitrite	> 0.1
ferrous salt	> 1.0
ferric salt	> 1.0
residual chlorine	> 1.0
chloride	> 1.0
released chlorine	> 1.0

Interferences with Tests

The test for sulfates may be affected by the presence of sulfites and sulfides in the sample. Sulfites and sulfides can be oxidized and precipitate with the sulfates to give a high result.

With the test for sulfites, other reducing agents, such as sulfides and ferrous iron, will cause high results. Upon acidification, nitrite in the sample will oxidize all or part of the sulfite. Proteins in the sample will tend to prevent the starch-iodine reaction, and cyanides will react with the iodine in the sample.

The test for nitrites is affected by copper which catalyzes the decomposition of the diazonium salt. The azo dye reacts with peroxides to form azoxy compounds, sodium hydroxide to form hydrazo compounds, and tin chloride to form amines. Also chlorine bleaches the azo dye, thus causing low results.

Copper, chromium, nickel, and zinc form complexes with 1,10 phenanthroline and thus consume the reagent. Therefore, the 1,10 phenanthroline may have to be in excess (about 10 times iron concentration) for the ferrous (or ferric) salts test.

The tests for residual and released chlorine are not specific because other halogens are also detected. Even ferric iron may oxidize the iodide ions in the test.

Also the test for chloride is not specific since bromide, iodide, and sulfide may precipitate with the chloride to give a high result.

APPARATUS

All glassware must be thoroughly cleaned to assure the removal of interfering substances. Detergents may be used if cleaning is followed by thorough rinsing with distilled water.

The apparatus requirements are as follows:

1. Test tubes, 16 x 150 mm
2. Test tube rack
3. Reagent bottles : 2-100 ml, 1-200 ml, 2-250 ml, 5-500 ml
(one of which is a dark bottle), 1-1000 ml
4. Dropper bottles
5. Volumetric flask: 1-100 ml, 2-200 ml, 1-250 ml, 2-500 ml,
7-1000 ml
6. Graduates: 10 ml, 100 ml and 500 ml

7. Balances: Trip or Triple Beam and Analytical
8. Filter paper
9. Pipets: 5-1 ml, 1-5 ml, 1-50 ml

REAGENTS

Introduction

Since these preliminary tests are qualitative in nature, the concentrations of all reagents, except the standard solutions, are approximate. The analyst should prepare the standards with care, however, as they serve to familiarize him with the hue and density of color produced by the limit concentration of impurities.

Chemical Requirements

The following chemicals are ACS, Reagent grade:

1. barium chloride
2. sodium sulfite
3. concentrated hydrochloric acid
4. potassium iodide
5. potassium dichromate
6. Thyodene
7. sodium nitrite
8. acetic acid, glacial
9. sulfanilic acid
10. 1-naphthylamine [or 1-naphthylamine hydrochloride or
N-(1-naphthyl) ethylenediamine dihydrochloride]
11. ferrous sulfate, crystal
12. 1,10 phenanthroline [or 1,10 dipyridyl]
13. ferric chloride, lump
14. hydroxylamine hydrochloride

- 15. iodine
- 16. concentrated sulfuric acid
- 17. sodium chloride
- 18. silver nitrate

Preparation of Solutions

All solutions are prepared with distilled water which was distilled from a block tin or all-glass still, contains less than 0.01 mg/l copper, and free of chlorine, chloramines, caustic alkalinity, organic materials, and acids. The solutions are prepared in the following manner:

1. Group A - standard stock solution: Dissolve 0.3697g Na_2SO_4 in 1000 ml flask with distilled water and dilute to mark. This stock solution contains 250 ppm sulfate ion and is stable for at least one week.
2. Group A - standard working solution: Pipet 1 ml of stock solution into 500 ml flask and dilute to mark. This working solution contains 0.5 ppm sulfate ion and should be prepared day to be used.
3. Group A - test solution: Dissolve 5 g BaCl_2 in 500 ml reagent bottle with distilled water and dilute to about 500 ml. This solution is stable for at least one week.
4. Group B - standard stock solution: Dissolve 0.3936g Na_2SO_3 in 1000 ml flask with distilled water and dilute to mark. This stock solution contains 250 ppm sulfite ion and should be prepared each day to be used.

5. Group B - standard working solution: Pipet 1 ml of stock solution into 250 ml flask and dilute to mark. This working solution contains 1.0 ppm sulfite ion and should be prepared each day to be used.
6. Group B - test solution #1: Prepare daily by dissolving 2g KI in 250 ml reagent bottle with about 100 ml of distilled water. Add 10 ml conc. HCl and dilute to about 250 ml.
7. Group B - test solution #2: Dissolve 2g $K_2Cr_2O_7$ in 500 ml reagent bottle with distilled water and dilute to about 500 ml. This solution is stable for about one week.
8. Group C - standard stock solution: Dissolve 0.6000g $NaNO_2$ in 1000 ml flask with distilled water and dilute to mark. This stock solution contains 400 ppm nitrite ion and should be prepared each day to be used, however, if stored in a refrigerator, the stock solution is stable for one week.
9. Group C - standard working solution: Pipet 1 ml of stock solution into 100 ml flask and dilute to mark. This working solution contains 4.0 ppm nitrite ion and should be prepared each day to be used.
10. Group C - test solution: Dissolve 10 ml acetic acid, 10g sulfanilic acid, and 1g 1-naphthylamine [or 1-naphthylamine hydrochloride or N-(1-naphthyl)ethylenediamine dihydrochloride] in 1000 ml reagent bottle with distilled water and dilute to about 1000 ml. Prepare daily.
11. Group D - standard stock solution: Dissolve 0.9955g $FeSO_4 \cdot 7H_2O$ in 1000 ml flask with distilled water and dilute to mark. This stock

solution contains 200 ppm ferrous iron and should be prepared day to be used.

12. Group D - standard working solution: Pipet 1 ml of stock solution into 200 ml flask and dilute to mark. This working solution contains 1 ppm ferrous iron and should be prepared each day to be used.
13. Group D - test solution: Dissolve 5g 1,10 phenanthroline (or 1,10 dipyridyl) in 500 ml reagent bottle with distilled water and dilute to about 500 ml. Prepare daily.
14. Group E - standard solution #1: Dissolve 0.9676g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1000 ml flask with distilled water and dilute to mark. This #1 standard solution contains 200 ppm ferric iron. Prepare daily.
15. Group E - standard solution #2: Pipet 50 ml of the above #1 standard solution into 200 ml flask and dilute to mark with distilled water. This #2 standard solution contains 50 ppm ferric iron. Prepare daily.
16. Group E - test solution: Dissolve 5g hydroxylamine hydrochloride in 500 ml reagent bottle with distilled water and dilute to about 500 ml. Prepare about each week.
17. Group F - standard solution: Dissolve about 1g iodine in distilled water and dilute to 1000 ml. Prepare about each.
18. Group F - test solution: Prepare daily by dissolving 2g KI in 250 ml reagent bottle with about 100 ml of distilled water. Add 5 ml conc. H_2SO_4 and dilute to about 250 ml.

19. Group G - standard stock solution: Dissolve .8243g NaCl in 500 ml flask with distilled water and dilute to mark. This stock solution contains 500 ppm chloride ion and is stable for about one week.
20. Group G - standard working solution: Pipet 1 ml of stock solution into 500 ml flask and dilute to mark. This working solution contains 1.0 ppm chloride ion and should be prepared each day to be used.
21. Group G - test solution: Dissolve 5g AgNO₃ in 500 ml dark-reagent bottle with distilled water and dilute to about 500 ml. Prepare about each week.
22. Group H - standard solution: May use either standard solution of Group F or standard stock solution of Group G.
23. Group H - indicator solution: Dissolve 5g Thyodene in 100 ml reagent bottle with distilled water and dilute to about 100 ml. This solution is stable for several weeks.
24. Group H - test paper: Impregnate ordinary filter paper, 1/4-inch wide strips, with Group F test solution and indicator solution immediately before use.

STANDARDIZATION

No special standardization is needed. However, the standard solutions mentioned under "Reagents" are analyzed along with the unknown samples. This allows the analyst to compare the color of an unknown to the color intensity of the known impurity at maximum tolerable concentration.

SAMPLE ANALYSIS

Test for Group A Substances (as sulfates)

Procedure:

Comment:

1. Pour equal volumes of sample (or standard working solution) and test solution into test tube.

1. A cloudy white solution indicates Group A and/or Group B.

Test for Group B Substances (as thiosulfates, sulfites)

Procedure:

Comment:

1. Pour equal volumes of sample and test solution #1 into test tube.
If sample turns cloudy whitish yellow, stop at this point.
If sample remains clear, go on to step 2.
2. Add a small amount of Thyodene powder to this clear mixture and to another test tube with equal volume of test solution #1. If sample solution remains clear, go to step 3.
3. Perform a dropper-titration with each solution using test solution #2 until each solution has the yellow color of the test solution #2.

1. a) Use sulfite standard working solution as a guide.
b) Cloudy whitish yellow indicates thiosulfates or the like.
2. a) Test solution #1 may turn pale blue due to some iodine created during preparation of the solution.
b) If mixture with sample turns pale blue, sulfite is not present.
3. a) The test solution #1 should turn yellow color with only 1 to 2 drops of titrant.
b) If the sample solution turns blue with 1 to 2 drops of titrant and yellow after several drops, sulfite-type substances are present.

The amount of titrant used for the sample mixture must exceed the amount needed for test solution #1 for sulfite-type substances to be present.

4. If only a slight amount of sulfite-type substance is present, repeat test with aerated-diluted sample.
4. Sulfite-type substances may react and disappear upon aeration.

Test for Group C Substances (as nitrites)

Procedure

1. Pour equal volumes of diluted-aerated sample and test solution into test tube.
2. After a few minutes, look for the red color of an azo dye.

Comment:

1. a) Test may first be performed with undiluted sample.
b) Use dilution employed in DO determination.
a) Reagent reference blank may be needed.
b) Use nitrite standard working solution as a guide for limitation of nitrite concentration.
c) If Group B is present, this test shows a negative result.

Test for Group D Substances (as ferrous salts)

Procedure:

1. Pour equal volumes of diluted-aerated sample and test solution into test tube.

Comment:

1. a) Test may first be performed with undiluted sample.
b) Use dilution employed in DO determination.

2. After a few minutes, inspect the solution for the formation of an orange-red color, indicative of the presence of ferrous salts.
- c) Use Group D standard working solution as a guide.
2. a) Sample may need filtering to see to color.
- b) If Group B is present, this test shows a negative result.
- c) The interference from nitrite ion may be eliminated by adding an excess of test solution.

Test for Group E Substances (as ferric salts)

1. Treat a portion of sample (standard solutions #1 and #2, and diluted-aerated or non-diluted quench water) as directed in steps 1 and 2 of the Test of Group D Substances.
1. May use same sample portion employed in the Test for Group D Substances.
2. Add to each test tube an equal volume of test solution.
3. After a few minutes, inspect the solution for the formation of an orange-red color that is deeper than the color formed in the Group D Test.
3. a) Comments for step #2 of test for Group D apply here also.
- b) If the intensity of the color greater than standard solution #1 but less than #2, the Modified Winkler Method can be employed provided the potassium fluoride is employed.

Test for Group F. Substances (as residual chlorine)

Procedure:

1. Pour equal volumes of undiluted sample (or standard) and test solution into a test tube. If the sample mixture turns cloudy-whitish-yellow (as in Group B test) stop at this point. If the solution is clear, go to step 2.
2. To the clear sample (and reagent blank) add a small amount of Thyodene powder.
3. If a blue color (deeper than the blank) forms, chlorine-like substance is present.
4. If the test is positive, repeat with a diluted-aerated sample.

Comment:

1. a) More readily available iodine used as a standard instead of chlorine.
b) Use a reagent (test solution) blank.
c) Cloudy-whitish-yellow is indicative of thiosulfate.
2. Test solution may turn pale blue due to some iodine created during preparation of the solution.
4. Chlorine-like substances may dissipate upon aeration.

Test for Group G Substances (as chlorides)

Procedure:

1. Pour equal volumes of diluted-aerated sample (or standard) and test solution into test tube.

Comment:

1. Cloudy white solution indicates Group G. A heavy white precipitation indicates possible interference from Group H substances.

Test for Group H Substances (as released chlorine)

Procedure:

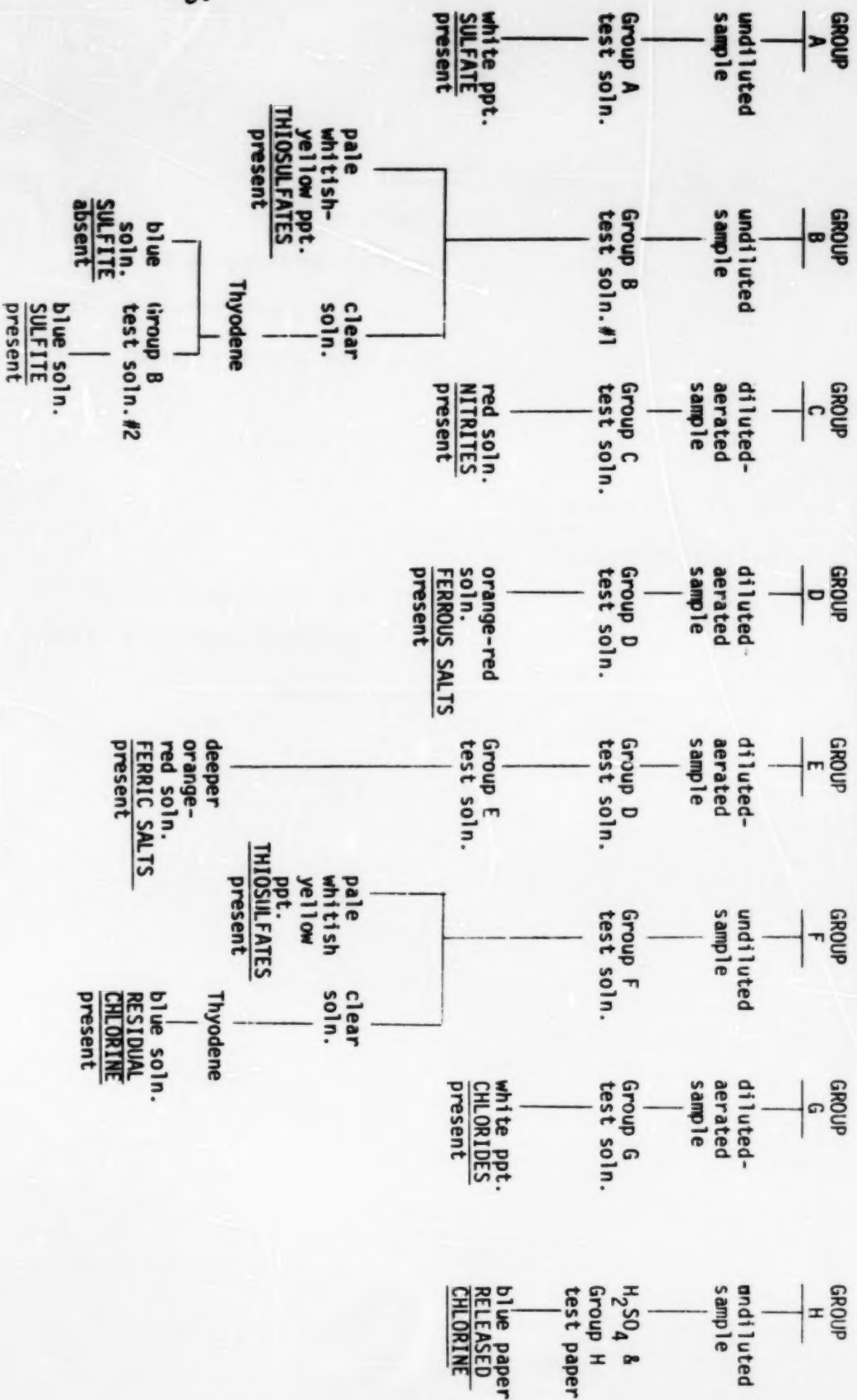
1. Fill half of a test tube with sample (or standard).
2. Pour 1 to 2 ml of conc. H_2SO_4 into test tube.
3. Immediately place test paper into upper half of test tube.
4. After a few minutes, look for the paper to turn blue.

Comment:

1. This test need only be performed if the test sample showed no Group F and high amounts of Group G.
4. Blue color indicates a free halogen which interferes with the Modified Winkler Method.

TABLE 1

FLOW CHART FOR TESTS FOR GROUPS A-H SUBSTANCES



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